

## FULLY BLEACHED SULFITE CHEMICAL PULP, A PROCESS FOR THE PRODUCTION THEREOF AND PRODUCTS DERIVED THEREFROM

The present invention relates to a completely bleached sulfite chemical pulp, a process for the production thereof and products made of this pulp (nonwovens or paper, especially tissue paper).

### Background Art

In the production of paper, we differentiate between chemical pulp and mechanical pulp.

According to DIN 6730, chemical pulp is a fibrous material obtained from plant raw materials from which most non-cellulose components have been removed by chemical pulping without substantial mechanical post-treatment. In case of chemical pulping processes such as the sulfite or sulfate (Kraft) process, primarily the lignin components and the hemi-cellulose components are dissolved from the wood to varying degrees depending on the field of application of the chemical pulp. The result is a fibrous material consisting primarily of cellulose.

Mechanical pulp is the general term for fibrous materials made of wood entirely or almost entirely by mechanical means, optionally at increased temperatures. Mechanical pulp is subdivided into the purely mechanical pulps (groundwood pulp and refiner mechanical pulp) as well as mechanical pulps subjected to chemical pretreatment: chemo-mechanical pulp (CMP), such as chemo-thermomechanical pulp (CTMP).

Chemical and mechanical pulp are also known by the general designation pulp.

The strength of papers made from chemical pulps (hereinafter abbreviated as "strength of the chemical pulp") is substantially determined by the pulping degree of the wood used as starting material. The binding ability of the fibers first increases as more and more lignin is removed and reaches a maximum at a lignin content of about 10%. At this residual lignin content, the fibrous material has good stiffness and resistance to tearing along with a high

binding ability. As delignification proceeds, the overall strength of the chemical pulp decreases due to the strong attack of most of the pulping chemicals on the carbohydrate portion (cellulose and hemicellulose) of the wood.

However, such extensive delignification is accompanied by losses in yield so that, for many years, there have been efforts to develop pulps having higher contents of residual lignin:

- high-yield chemical pulps, according to DIN 6730 a chemical pulp primarily pulped chemically, but subsequently subjected to mechanical defibration;
- semi-chemical pulp, a pulp according to DIN 6730 obtained from plant raw materials by chemical pulping from which only part of the non-fibrous components have been removed and which is subjected to mechanical post treatment; and
- chemi-mechanical pulps (CMP, CTMP, as defined above).

In the meantime, the recovery of primary fibers has focused, on the one hand, on the production of mechanical pulps in very high yields by addition of 1% to 5% maximum of sodium sulfite such that hydrophilizing occurs by introducing sulfonic acid groups in conjunction with a low dissolving rate of the wood components, and on the other hand, on the production of full chemical pulps according to the sulfate process.

If chemical pulp recovered by the sulfate process (called "Kraft pulp" or "sulfate chemical pulp") is to be used for producing products with a high degree of brightness, the lignin must be removed completely, since even small amounts of residual lignin are discolored due to chemical changes in the lignin structure (primary condensation). This is largely carried out in a pulping process. Any residual lignin still present is then removed in several bleaching steps.

The native lignin is less discolored by the acidic sulfite process. For this reason, it was possible to use high-yield chemical pulps made by acidic or semi-acidic sulfite processes in

unbleached form for special applications. If a higher degree of brightness was required, such chemical pulps were also bleached in a delignifying manner with chlorine and bleaching agents containing chlorine. However, these products were unable to satisfy the ever-increasing optical demands. In addition, environmental concerns about bleaching agents containing chlorine and chemical pulps containing chlorine led to a situation where industrial-level production of high-yield chemical pulps was not pursued. Furthermore, less expensive recycling paper has increasingly been used in paper production.

However, delignifying bleaching of chemical pulps often has the disadvantage that chemicals used for bleaching also attack cellulose fibers to a considerable extent, thus reducing the strength of chemical pulps.

Therefore up until now, it has been thought that pulps of sufficient strength and of a high degree of brightness could only be obtained by pulping to low kappa values followed by bleaching. This also applies to the sulfite pulping process.

A summary of the development of acidic sulfite pulping processes for preparing semi-chemical pulps is found in R. Runkel and K.F. Patt, "*Halbzellstoffe*" (Semichemical Pulps), Günther-Stalb Verlag, Biberach 1958, pages 35 – 37 and pages 95 – 96. The production of high-yield chemical pulps, semichemical pulps and chemi-mechanical pulps according to the sulfite process is also described in "S.A. Rydholm, *Pulping Processes*, Interscience Publishers, New York, London, Sydney, 1965, pages 418 – 420".

In addition, G. Jayme, L. Broschinski, W. Matzke (in *Das Papier* 18, 1964, pages 308 through 314) present a general survey of high-yield chemical pulps and give a detailed description of rapid pulping in the vapor phase with magnesium bisulfite at a maximum temperature of 180°C over a period of 8 to 20 minutes.

DE-A-1- 517 219 relates to the preparation of a (high-yield) sulfite chemical pulp. Wood raw material is pulped with an aqueous solution containing sulfite and/or bisulfite ions as well as sodium, potassium, magnesium, or ammonium ions. The pH of the solutions at onset of pulping is 3.0 to 7.0, preferably 3.7 to 5.0. The maximum pulping temperature is 140° to 190° C, preferably 150° to 170° C. The entire pulping process takes more than 400

minutes. The residence time at the maximum temperature is 30 to 200 minutes. Pulping is carried out at a chlorine number of the finished chemical pulp in the range of 15 to 32, the pulped material then being subjected to controlled defibration and/or defibration/refinement. After that, fines are removed in an amount of 0.2 to 7 % of the amount of the chemical pulp.

In unbeaten form (freeness value °SR = 14.5 – 15) the material thus obtained has a breaking length of 6.3 km. The chemical pulp is not bleached.

US 4,634,499 and US 4,734,162 each relate to processes for preparing a chemical pulp from hardwood which is especially suitable for the preparation of tissue papers. Pulping is carried out with ammonium sulfite, first at less than 110° C, then at a maximum temperature of 140° C to 155° C at a pH of about 2 to 3. The chemical pulp is not subjected to an additional bleaching step.

EP 0 287 960 A relates to a process for preparing a hemicellulose hydrolysate and a special chemical pulp by a two-step process, wherein

- a first step comprises pre-hydrolysis of the ligno-cellulosic materials, for example, with water, a mineral acid, sulfur dioxide, sulfite pulping liquor, and sulfite waste liquor, at a temperature of 100° to 180° C and over a hydrolysis period of 10 to 200 minutes, and
- a second step in which the lignin contained in the pre-hydrolysed material is dissolved occurs by means of neutral sulfite pulping with addition of anthraquinone as the catalyst, the initial pH being at least 10. The temperature is preferably 160° to 180° C and the treatment time 100 to 200 minutes.

Following the second step, the resulting ligno-cellulosic material is mechanically defibrated and optionally bleached.

Yields obtained in this manner range from 37.0 % to 45.7 % based on the wood used, the

kappa number ranges from 17.2 to 48.1, and the degree of brightness (ISO value) at 48.2 to 87.1.

GB-1,546,877 B relates to a CTMP (chemo-thermomechanical pulp) which is suitable for absorbant products such as tissue paper, and, additionally, has a light color. Yields at 85 % to 95 % are well above the common values for high yield pulps. The production process comprises the following steps:

- washing of a ligno-cellulosic material with water
- impregnation and pulping with a liquid containing sulfur dioxide at a temperature of 100° to 170° C, preferably at a pH of 5 to 11.
- partial defibration of the resulting material by mechanical means with simultaneous bleaching.

Suitable bleaching chemicals are alkali metal peroxides such as sodium peroxide or hydrogen peroxide, or reducing bleaching agents such as dithionite, hydroxyl amine, thiourea, or thioglycolic acid.

An essential feature of the resulting chemical pulp is a content of at least 10 % by weight of sulfonated fiber bundles, each consisting of two to four individual fibers.

This British patent does not address the strength properties of the chemical pulp obtained. The description of the patent further points to non-satisfactory degrees of brightness of the resulting chemical pulp.

EP 0 446 110 A describes a process for bleaching chemical pulps (yield ranges approx. 85 to 90 %), which are obtained mechanically (mechanical pulp), optionally combined with chemical methods (chemomechanical pulp) and/or thermal methods. This bleaching process comprises the following steps:

- pretreatment of (mechanical or chemomechanical) pulp with a complexing agent for metal ions followed by a washing step
- treatment with sulfite and a more electronegative reducing agent at a pH between 7 and 12.5 followed by a washing step
- bleaching treatment with hydrogen peroxide in an alkaline environment.

According to example 1, this process produces degrees of brightness of 83.9% ISO.

However, all processes known from the prior art for preparing pulps having a high degree of brightness have disadvantages. In particular, insufficient resistance against fiber collapse and poor strength of individual fibers is observed in the pulp obtained. At low degrees of beating, known pulps often have strength values insufficient for preparation of tissue products.

Bleached mechanical pulps and bleached chemomechanical pulps have the further disadvantage of an unstable degree of brightness. This is due to the fact that the bleaching chemicals convert chromophoric groups of the lignin into non-chromophoric groups, which however are unstable. This type of reduction in the degree of brightness (discoloration) may be induced either by light or heat.

A disadvantage of known chemical pulps is their chlorine content and/or formation within the bleach of soluble reaction products containing chlorine, which is environmentally undesirable.

Therefore, it is the object of the present invention to make available a pulp that has further properties in addition to a high and durable optical quality, making it particularly suitable for the production of nonwovens and paper (products), in particular tissue products.

A further aspect of the invention is to make available a process for producing such pulp.

Finally, a further object of the present invention is to make available pulp based paper or nonwovens and/or products which are characterized by both resistance to mechanical stress and high quality of appearance.

It is a further object of the invention to make available an environmentally compatible process for producing environmentally compatible pulp and derivative paper and/or nonwoven products.

## SUMMARY OF THE INVENTION

These objects are achieved by:

- a process for producing a chlorine-free bleached sulfite chemical pulp comprising the following steps:
  - delignification of chips (commonly woodchips) from lignocellulosic material by a sulfite pulping process, in particular, in the presence of magnesium until the defibration point has been attained, and
  - bleaching of the resulting fibrous material in a chlorine-free bleaching sequence comprising at least one bleaching step using an oxidizing agent in the presence of a base;
- chlorine-free bleached chemical pulp obtainable by a sulfite pulping process followed by chlorine-free bleaching, characterized in that it has an ISO degree of brightness of at least 83 % and a strength, expressed as breaking length, of at least 6 km (measured according to Zellcheming V/12/57), determined with a test sheet (ISO 5269-2, August 1998) produced from the pulp without beating the same, and
- paper and nonwovens obtainable from this pulp.

## DETAILED DESCRIPTION OF THE INVENTION

### Process

In the first step of the process according to the invention, chips (commonly woodchips) from ligno-cellulosic material are partially delignified in a sulfite pulping process, in particular in the presence of magnesium, until the point of defibration of the material is attained.

The point of defibration is the point in time during the pulping at which the fibers subjected to chemical delignification may readily be separated into individual fibers without mechanical defibration. Once the point of defibration has been reached, the individual fibers are collected generally by pumping off the pulped lignocellulosic material out of the cooker. The kappa value of the resulting pulp depends on the type of wood, the degree of pulping, as well as on the chemical system that was applied. Preferably, the partially delignified fibrous material obtained from the first step has a kappa value (according to DIN 54357, August 1978) of 50 to 75, in particular 60 to 70. This is the case, in particular, for spruce or pine.

One advantage of the sulfite process used according to the invention is that the point of defibration is obtained at considerably higher residual lignin contents and yields than in the sulfate pulping process. This is due to the fact that in the initial pulping phase, sulfite solutions prefer to dissolve lignin in the middle lamella of the wood cells, and thereby the bonding between the wood cells is lost. This results in a fiber surface of relatively low residual lignin content. The largest part of the yet remaining lignin is located in the central layer of the cell wall (S2) (on the structure of a wood cell, see *e.g.* Figure 20.2, page 509 in T.P. Nevell and S. Haig Zeronian, *Cellulose Chemistry and Its Applications*, John Wiley & Sons). In contrast to the residual lignin content of sulfate pulp, the residual lignin content of the pulp resulting from the sulfite process, in particular the acidic sulfite process has not only relatively few chromophoric groups, but it is also less condensed and therefore more reactive.

The term "ligno-cellulosic material" includes all materials containing cellulose and lignin as main components, typically wood. In (dry) wood, the lignin content is generally at least 20 wt.-% (hardwood about 22 wt.%, conifers 27 – 33 wt.-%). Usually, the cellulose content of wood is at least 40 wt.-%, generally 40 to 50 wt.-%. Both softwood from conifers and



hardwood from deciduous trees may be used in the process of the invention. Examples for suitable kinds of wood comprise spruce, pine, aspen, beech, birch, maple, poplar, and oak. In addition, eucalyptus is especially suitable as a source of fibers for tissue papers. The use of spruce and beech is especially preferred.

Prior to pulping, the ligno-cellulosic material used is roughly chopped into chips. The size of the chips may vary and ranges for example from 1 to 5 cm in breadth and length, with a thickness of up to 1 cm.

Pulping (first step) is carried out with an acidic sulfite solution in a known manner, *e.g.* with an aqueous solution containing sulfite and/or bisulfite ions as well as sodium, potassium, magnesium, or ammonium ions. Suitable methods are described in depth in G. A. Smook, M. J. Kocurek, *Handbook for Pulp and Paper Technologists*, Tappi, Atlanta, 1982, pages 58 through 65. Preferably, the chemical pulping occurs in a single step, *i.e.* without sudden (as contrast to gradual) changes in conditions of the process such as pH. The entire pulping process does not require any additional mechanical means.

Chips of lignocellulosic material may be pulped in alkaline, neutral, or acidic conditions, however, preferably in an acidic environment with sulfite. Pulping at a pH of 1 to 5, especially 1.2 to 4.0 is particularly preferred.

In a particularly preferred embodiment, pulping is performed with an aqueous solution containing sulfite and/or bisulfite ions as well as magnesium ions. One advantage of this variant is the possibility of recovering MgO and SO<sub>2</sub> from the pulping waste liquors by thermal decomposition and recycling them to the pulping process. The pulping temperature preferably ranges from 130° to 165° C, in particular 135° to 150° C. Until a maximum temperature of 130° to 150° C is attained, heating should preferably be carried out over a period of 30 to 120 minutes.

Then, the temperature is maintained at the maximum temperature preferably for a time period of 120 to 300 minutes. A time period of 30 to 60 minutes is preferred for cooling from the maximum temperature ( $T_{\max}$ ) to room temperature.

Total pulping time (heating + pulping at  $T_{\max}$  + cooling) ranges preferably from 180 to 480 minutes.

The  $\text{SO}_2$  content of the pulping solution relative to the dry weight (see Examples for its determination) of the lignocellulosic material used preferably equals 5 to 30 % by weight, in particular 15 to 24 % by weight. The proportion of magnesium if present, relative to the dry weight of the lignocellulosic material, expressed as  $\text{MgO}$ , preferably equals 4 to 10 % by weight, in particular 6 to 7.5 % by weight.

According to the invention, addition of further pulping chemicals such as, for example, anthraquinone is not required, but may be used in alkaline sulfite pulping processes.

The lignocellulosic material-to-liquor ratio preferably ranges from 1:3 to 1:5, especially from 1:3.5 to 1:3.7, relative to the dry weight of the lignocellulosic material.

The first step of the pulping process according to the invention results in an unbleached chemical pulp (hereinafter also referred to as "fibrous material"), which is then transferred to the bleaching sequence.

The yield of unbleached chemical pulp relative to the dry weight of the ligno-cellulosic material used is greater than 50 % by weight, preferably at least 55 % by weight, for example, about 60 % by weight.

The degree of brightness of the material thus obtained is usually equal to 35 to 60 % ISO, preferably 40 to 55 % ISO.

Preferably, the unbleached chemical pulp has the following strength parameters, each measured according to ISO 5269-2; August 1998, on test sheets having a basis weight of about 80 g/cm<sup>2</sup> using a standard climate according to DIN EN 20187 (see description in the Examples). All of the following values are based on unbeaten chemical pulp which

corresponds to a freeness value (°SR, measured according to DIN-ISO 5267/1; March 1999) of approx. 12 to 15:

- a breaking length (dry, measured according to Zellcheming V/12/57) of at least 9 km, more preferably at least 10 km, especially 10 to 11 km, and
- a tear strength (dry, see Examples, measured according to Elmendorff; DIN 53128) relative to 100 g/m<sup>2</sup>, of at least 70 cN, more preferably at least 75 cN, especially 85 to 100 cN.

The sulfite pulping process used as the first step of the process of the invention has the advantage over the sulfate process of producing a pulp having a relatively light color even at higher residual lignin contents.

This intermediate, which likewise is a part of the invention, as well as the process steps producing it, is then subjected to bleaching in one or more steps.

Prior to bleaching, the chemical pulp resulting from the first stage (delignification) is separated from the cooking liquor in a known manner, *e.g.* it may be filtered and optionally washed (usually with water).

The common feature of each bleaching sequence used according to the invention is bleaching with a chlorine-free oxidant, in the presence of a base in a so-called "first bleaching step". The entire bleaching sequence is carried out with chlorine-free agents. The terms "chlorine-free bleaching sequence" and "chlorine-free bleaching chemicals" mean that the bleaching chemicals contain no chlorine, neither elemental chlorine, nor bonded chlorine such as, *e.g.* in chlorine dioxide.

The entire bleaching sequence is preferably carried out without additional mechanical pulping means, *i.e.* defibration means.

The base used in the first bleaching step is preferably the same base that is used in pulping. This makes it easier to close water cycles, since the filtrate from the washer after the first bleaching step may be used for washing in the washer after the pulping step. Furthermore, by using the same base, preferably one containing magnesium, the resulting bleach waste liquors may be disposed together with the cooking waste liquors or at least partially recycled.

Sodium hydroxide, magnesium oxide ( $\text{MgO}$ ), and/or magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) are preferred bases. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is a preferred oxidant. The amount of oxidant is preferably 35 to 60 kg/t, in particular 40 to 55 kg/t, relative to the dry weight of the fibrous material used. The amount of base used generally ranges from 10 to 20 kg/t relative to the dry weight of the fibrous material used.

The first bleaching step is preferably conducted at a temperature of  $60^\circ$  to  $80^\circ$  C. The preferred pH range is from 8.5 to 9.5. The duration of this bleaching step is preferably 240 to 420 minutes.

The effect of this first bleaching step may be intensified by using oxygen. Preferably oxygen is used in an amount of 0.5 % to 3 % relative to the dry weight of the fibrous material used.

This first bleaching step is preferably combined with at least one other (so-called "second") bleaching step which is also conducted with an oxidant, in the presence of a base. In addition to the oxidant mentioned above (hydrogen peroxide), the use of peracetic acid (PAA), preferably in a pH range from 7 to 9, is especially suitable for this second optional bleaching step. The preferred base is sodium hydroxide ( $\text{NaOH}$ ) or magnesium oxide ( $\text{MgO}$ ) (where hereinafter the term "Magnesium oxide ( $\text{MgO}$ )" also includes magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ). Both oxidant and base may be used in the same amounts set forth above. Duration and temperature of this bleaching step may also correspond to those of the first bleaching step.

The advantage of a peracetic acid step (magnesium oxide as base) as the second optional bleaching step is the fact that additional waste water cycles may be closed in order to minimize waste.

In particular, if using peroxides or peracids in the first or second (optional) bleaching step, bleaching abilities may be improved by first treating the fibrous material with a complexing agent. According to the invention, examples of suitable complexing agents are nitrogen-containing organic compounds, in particular nitrogen-containing polycarboxylic acids, nitrogen-containing polyphosphonic acids, and nitrogen-containing polyalcohols. Examples of nitrogen-containing polycarboxylic acids are diethylenetriamine pentaacetic acid (DTPA), ethylenediamine tetraacetic acid (EDTA), and nitrilo-triacetic acid (NTA). Diethylenetriamine pentamethylenephosphonic acid (DTPMPA) and diethylenetriamine pentaphosphonic acid are examples of nitrogen-containing polyphosphonic acids. Furthermore, one may also use other complexing agents such as polycarboxylic acids, *e.g.* oxalic acid, citric acid or tartaric acid, or phosphonic acids. Preferred complexing agents are: DTPA, DTPMPA, and EDTA.

Preferably, complexing agent may be added in the amount of 0.5 to 3 kg/t relative to the fibrous material used. Preferably, the complexing treatment is performed at approx. 60° C.

- In one embodiment, the complexing treatment is carried out in a weakly acidic environment (hereinafter referred to as “Q”).
- In order to activate the residual lignin content of the fibrous material, one may also use an oxidant in an acidic environment along with the complexing agent. For this purpose, peracetic acid (hereinafter referred to as “Q/PAA”) and ozone are particularly suited.
- In an additional, particularly preferred embodiment (referred to as an acidic wash or “A<sub>Q</sub>”), one sets the pH of the pulp suspension at a value of 3 or less, *e.g.* by addition of H<sub>2</sub>SO<sub>4</sub>. In this manner, one may dissolve MgO that has precipitated onto the pulp or into the suspension. After setting the pH value, one adds the complexing agent to the suspension. This form of complexing treatment is particularly suited as a first step of the bleaching sequence, or if it has been preceded by at least one bleaching step in the presence of MgO as base.

The second (optional) bleaching step may be followed by additional oxidizing bleaching steps with chlorine-free oxidants in the presence of base. After treatment with peracetic acid, a third oxidizing bleaching step is preferably performed using hydrogen peroxide in the presence of sodium hydroxide as base. This third oxidizing bleaching step is preferably performed under the same conditions as those described in the first and second bleaching steps.

The oxidizing bleaching steps are preferably combined with a so-called “reducing bleaching step” using a reducing bleaching agent. In a preferred embodiment, a reducing bleaching step concludes the entire bleaching sequence. In another preferred embodiment, the bleaching sequence comprises a first oxidative bleaching step, followed by reducing bleaching step, and then an additional oxidative bleaching step. Bleaching agents that are suitable for the reducing bleaching step include water-soluble dithionite salts, hydroxylamine, thiourea, thioglycolic acid, borohydride (e.g. sodium borohydride), or formamidinosulfinic acid. Especially preferred is the use of formamidinosulfinic acid or dithionite, particularly sodium dithionite.

The amount of reducing agent used in the reducing bleaching step preferably ranges from 5 to 15 % by weight relative to the amount of fibrous material used. This reaction is preferably performed at a pH ranging from 9 to 11. Preferably, sodium hydroxide or magnesium oxide is used to set the pH. Magnesium oxide has the advantage that the waste of this step may be disposed together with pulping waste liquor. The preferred temperature for the reaction is in the range of 80° to 95° C. The reaction preferably takes from 60 to 90 minutes.

Selection and sequence of the bleaching steps may be varied, where with multi-step bleaching sequences it is preferred to begin the bleaching sequence with an oxidative bleaching of the type  $P_{MgO}$  (bleaching step with hydrogen peroxide in the presence of  $MgO$  as base), optionally in the presence of oxygen ( $OP_{MgO}$ ), and to conclude the bleaching sequence with a reducing bleaching step.

The total residence time for all oxidizing and/or reducing bleaching steps (including complexing treatments) ranges preferably from 700 to 1200 minutes.

Following each individual step of the bleaching sequence (including complexing treatments), the fibrous material is preferably separated from the bleaching solution, *e.g.* by filtration, and washed. In this manner, the consumption of chemicals in bleaching may often be reduced. By washing upon completion of the bleaching sequence, the purity of the pulp according to the invention may be increased. Furthermore, it is preferred to work countercurrent, *i.e.* to wash the completely bleached fibrous material with clean water and to use the resulting wash water for pulp of the previous bleaching step or steps. Finally, the wash water from the washing following the first bleaching step is preferably used for washing the pulp following the pulping process. It is possible in the cases described above to use fresh water in addition to the wash water that is led in countercurrent.

Preferred bleaching sequences are as follows:

- 1)  $A_Q - (P_{MgO} \text{ or } OP_{MgO}) - Q - P_{NaOH} - (FAS_{NaOH} \text{ or } Y),$
- 2)  $A_Q - (P_{MgO} \text{ or } OP_{MgO}) - Q - PAA_{NaOH} - P_{NaOH} - (FAS_{NaOH} \text{ or } Y),$
- 3)  $Q - (P_{MgO} \text{ or } OP_{MgO}) - Q - PAA_{MgO} - P_{NaOH} - (FAS_{NaOH} \text{ or } Y),$
- 4)  $A_Q - (P_{NaOH} \text{ or } OP_{NaOH}) - Q - P_{NaOH} - (FAS_{NaOH} \text{ or } Y),$
- 5)  $Q/PAA - (P_{MgO} \text{ or } OP_{MgO}) - Q/PAA - FAS_{MgO} - P_{NaOH}, \text{ or}$
- 6)  $Q - P_{MgO} - A_Q - P_{NaOH} - FAS_{NaOH}$
- 7)  $Q - P_{MgO} - Q - P_{NaOH} - FAS_{NaOH}$

symbols meaning the following:

$A_Q$	acid wash with complexing treatment
$Q$	complexing treatment
$Q/PPA$	complexing treatment with concurrent activation of fiber surface with peracetic acid

$P_{NaOH/MgO}$	bleaching step with hydrogen peroxide in presence of NaOH or MgO as base
$OP_{NaOH/MgO}$	bleaching step with hydrogen peroxide in the presence of oxygen and NaOH or MgO as base
$PAA_{NaOH/MgO}$	bleaching step with peracetic acid in the presence of NaOH or MgO as base
$FAS_{NaOH/MgO}$	reducing bleaching step with formamidosulfinic acid in the presence of NaOH or MgO.
Y	reducing bleaching step with dithionite.

Based on the most recent knowledge, bleaching sequences 6 and 7 represent the best mode for practicing the invention.

## Pulp

In the manner described above, one may obtain bleached chemical pulp according to the invention. This pulp has the properties of a chemical pulp that is obtained by a sulfite pulping process, in particular a magnesium (bi)sulfite process, and that is then bleached without the use of chlorine or chlorine-containing chemicals. It has a brightness of at least 83% ISO and is further characterized by a breaking length (dry) of at least 6 km, preferably at least 7 km, more preferred at least 8 km, in particular at least 9 km, e.g. 10 km [measured (according to Zellcheming V/12/57) on a test sheet made from unbeaten pulp (freeness of 12 to 15° SR measured according to DIN-ISO 5267/1; March 1999) basis weight of approx. 80 g/m<sup>2</sup>, produced according to ISO 5269-2; August 1998, in a standard climate according to DIN EN 20187; November 1993)].

The degree of brightness is preferably at least 84 % ISO, particularly at least 85% ISO. For example, the degree of brightness may be 86 % ISO.

One advantage of the pulp according to the invention is that in contrast to mechanical pulp or chemomechanical pulp, its degree of brightness does not significantly decline during further processing.



The pulp according to the invention is substantially free of chlorine and/or chloride. Preferably, the pulp has an OX content of less than 30 mg/kg, or in particular, is free of OX. The OX content relates to the residual halogen organic compounds in the pulp, which may essentially be formed during bleaching and are measured in accordance with DIN 38414/18 and PTS-RH012/90.

Pulp that is low in OX or is OX-free, and/or products derived from such pulp are more environmentally compatible than pulp and pulp-derived products containing OX. This also applies to the production process. In order to close water cycles as much as possible, it is likewise preferred that only chlorine-free chemicals be used in pulp production, because that way a build-up of chlorine, chloride, and/or chlorine-containing substances may be avoided.

These properties of the pulp make it especially suitable for the production of tissue paper.

Preferably, (bleached, unbeaten) pulp according to the invention has

- a tear strength (dry, measured according to Elmendorff (DIN 53128) on test sheets described above under breaking length) relative to 100 g/m<sup>2</sup> of at least 90 cN, more preferably at least 95 to 105 cN.

The (bleached) pulp according to the invention preferably has a very low fiber bundle content of bundles having at least two fibers, i.e. preferably less than 5 % by weight, in particular less than 1 % by weight relative to the dry weight. It is more preferred for it to be free of such bundles.

In a preferred embodiment, the pulp is ground following the bleaching sequence. Preferably, it has a freeness value of more than 15, in particular more than 15 and simultaneously not more than 18 °SR. With an increased freeness value there is an increase in breaking length.

This additional surface treatment (beating), which has a favorable effect on the strength properties of the resulting paper/tissue paper, may preferably be brought about within the pulp refinement system of a paper/tissue paper machine. In another preferred embodiment, such surface treatment (beating) occurs as part of pulp production, *i.e.* while it is still at the pulp plant. A refiner is particularly suitable for this purpose. Fibrillation of the surface occurs during mechanical treatment of the pulp/water suspension. This treatment influences the static and dynamic strength properties.

Depending on the refiner's operating mode, the fibers are shortened (cut) or are fibrillated, which includes the separation of the outer layers of the fiber wall, this latter process substantially increasing the surface and bonding capacity of the fibers. The refiner operating mode associated with fibrillation is therefore preferred.

The residual lignin content of the bleached pulp according to the invention (measured according to DIN 54357, August 1978) ranges preferably from 10 to 30, more preferred from 15 to 25, in particular from 18 to 22. One may estimate the residual lignin content by multiplying the kappa numbers by 0.15. A kappa number of 20, which lies within the inventive range, thus corresponds to a residual lignin content of approx. 3 % by weight.

The process according to the invention thus makes it possible to a large extent to delignify lignocellulosic material without the aid of mechanical pulping means.

The average fiber length of the inventive bleached pulp ranges preferably from 1.8 to 2.2 mm (measured according to Kajaani using a Kajaani machine FS-200).

The water retention capacity of the pulp according to the invention ranges preferably from 130 to 150 %, in particular from 140 to 145 % (measured according to Zellcheming IV/33/57, as described in the Examples).

#### **Paper or Nonwoven (Product)**

The present invention also relates to paper or nonwoven comprising the bleached pulp according to the invention, preferably in the amount of at least 50 % by weight, in particular at least 80 % by weight, relative to the dry weight of the finished product.

The paper can be a packaging paper, a graphic paper or tissue paper. Preferably, the paper is a tissue paper.

The tissue paper or nonwoven may be one-ply or multiple-ply.

The German terms "Vlies" and "Vliesstoffe" are applied to a wide range of products which in terms of their properties are located between the groups, paper, paperboard, and cardboard on the one hand and the textile products on the other, and are currently summarized under the term "nonwovens" (see ISO 9092 - EN 29092). The invention allows the application of known processes for producing nonwovens, such as what are called air-laid and spun-laid techniques, as well as wet-laid techniques.

Nonwovens may also be called textile-like composite materials, which represent flexible porous fabrics that are not produced by the classic methods of weaving warp and weft or by looping, but by intertwining and/or by cohesive and/or adhesive bonding of fibers which may for example be present in the form of endless fibers or prefabricated fibers of a finite length, as synthetic fibers produced *in situ* or in the form of staple fibers. The nonwovens according to the invention may thus consist of mixtures of synthetic fibers in the form of staple fibers and the pulp according to the invention.

"Papers" are also planar materials, albeit essentially composed of fibers of a plant origin and formed by drainage of a fibrous-material suspension on a wire or between two continuously revolving wires and by subsequent compression and drainage or drying of the thus produced fibrous mat (*cf.* DIN 6730, May 1996). The standard restricts the range of mass per unit area (basis weight) for paper to a maximum of 225 g/m<sup>2</sup>.

Depending on the type of paper, the production process comprise also a sizing and/or smoothing step, along with the typical process steps of sheet formation, pressing, and drying described above.

Based on the underlying compatibility of the production processes (wet laying), "tissue" production is counted among the paper making techniques. The production of tissue is distinguished from paper production by its extremely low basis weight of normally less than 40 g/m<sup>2</sup> and its much higher tensile energy absorption index. (In processing inventive pulp to tissue paper, one generally selects a basis weight of 8 to 65 g/m<sup>2</sup>, especially 10 to 40 g/m<sup>2</sup>. The total basis weight of multiple-ply tissue products is preferably equal to a maximum of 65 g/m<sup>2</sup>.) The tensile energy absorption index is arrived at from the tensile energy absorption in which the tensile energy absorption is related to the test sample volume before inspection (length, width, thickness of sample between the clamps before tensile load). Paper and tissue paper also differ in general with regard to the modulus of elasticity that characterizes the stress-strain properties of these planar products as a material parameter.

A tissue's high tensile energy absorption index results from the outer or inner creping. The former is produced by compression of the paper web adhering to a dry cylinder as a result of the action of a crepe doctor or in the latter instance as a result of a difference in speed between two wires ("fabrics"). This causes the still moist, plastically deformable paper web to be internally broken up by compression and shearing, thereby rendering it more stretchable under load than an uncreped paper. Most of the functional properties typical of tissue and tissue products result from the high tensile energy absorption index (see DIN EN 12625-4 and DIN EN 12625-5).

One example of papers and paper products is represented by hygiene papers, particularly tissue papers and hygiene products (tissue products) made therefrom and which are *e.g.* used in personal grooming and hygiene, the household sector, industry, the institutional field in a wide variety of cleaning processes. They are used to absorb fluids, for decorative

purposes, for packaging or even as supporting material, as is common for example in medical practices or in hospitals.

Hygiene paper primarily includes all kinds of dry-creped tissue paper, as well as wet-creped paper and cellulose or pulp wadding.

The one-ply intermediate products originating from the paper-making machine and made of lightweight paper usually dry-creped on a yankee cylinder by means of a crepe doctor are generally described as "tissue paper" or more accurately raw tissue paper. The one-ply raw tissue may be built up of one or a plurality of layers respectively.

All one-ply or multi-ply final products made of raw tissue and tailored to the end user's needs, *i.e.* fabricated with a wide variety of requirements in mind, are known as "tissue products".

Typical properties of tissue paper include the ready ability to absorb tensile stress energy, their drapability, good textile-like flexibility, properties which are frequently referred to as bulk softness, a high surface softness, a high specific volume with a perceptible thickness, as high a liquid absorbency as possible and, depending on the application, a suitable wet and dry strength as well as an interesting visual appearance of the outer product surface. These properties allow tissue paper to be used for example as cleaning cloths, sanitary products (*e.g.* toilet paper), paper handkerchiefs, cosmetic wipes (facials) or as serviettes/napkins.

If tissue paper is to be made out of the pulp according to the invention, the process essentially comprises

- a forming that includes the headbox and the wire portion,
- b the drying portion (TAD (through air drying) or conventional drying on the yankee cylinder) that also usually includes the crepe process essential for tissues,

c the monitoring and winding area.

Paper can be formed by placing the fibers, in an oriented or random manner, on one or between two continuously revolving wires of a paper making machine while simultaneously removing the main quantity of water of dilution until dry-solids contents of usually between 12 and 35 % are obtained.

Drying the formed primary fibrous web occurs in one or more steps by mechanical and thermal means until a final dry-solids content of usually about 93 to 97 %. In the case of tissue making, this stage is followed by the crepe process which crucially influences the properties of the finished tissue product in conventional processes. The conventional dry crepe process involves creping on a usually 4.5 to 6 m diameter drying cylinder, the so-called yankee cylinder, by means of a crepe doctor with the aforementioned final dry-solids content of the raw tissue paper (wet creping can be used if lower demands are made of the tissue quality). The creped, finally dry raw tissue paper (raw tissue) is then available for further processing into the paper product or tissue paper product according to the invention.

Instead of the conventional tissue making process described above, the invention gives preference to the use of a modified technique in which an improvement in specific volume is achieved by a special kind of drying within process section b and in this way an improvement in the bulk softness of the thus made tissue paper is achieved. This process, which exists in a variety of subtypes, is termed the TAD (through air drying) technique. It is characterized by the fact that the "primary" fibrous web (like a nonwoven) that leaves the sheet making stage is pre-dried to a dry-solids content of about 80% before final contact drying on the yankee cylinder by blowing hot air through the fibrous web. The fibrous web is supported by an air-permeable wire or belt and during its transport is guided over the surface of an air-permeable rotating cylinder drum. Structuring the supporting wire or belt makes it possible to produce any pattern of compressed zones broken up by deformation in the moist state, resulting in increased mean specific volumes and consequently leading to an increase in bulk softness without decisively decreasing the strength of the fibrous web .

Another possible influence on the softness and strength of the raw tissue lies in the production of a layering in which the primary fibrous web to be formed is built up by a specially constructed headbox in the form of physically different layers of fibrous material, these layers being jointly supplied as a pulp strand to the sheet making stage.

When processing the raw fibrous web or raw tissue paper into the final product (third process section), the following procedural steps are normally used individually or in combination: cutting to size (longitudinally and/or cross cutting), producing a plurality of plies, producing mechanical ply adhesion, volumetric and structural embossing, ply adhesion, folding, imprinting, perforating, application of lotions, smoothing, stacking, rolling up.

To produce multi-ply tissue paper products, such as handkerchiefs, toilet paper, towels or kitchen towels, an intermediate step preferably occurs with so-called doubling in which the raw tissue in the finished product's desired number of plies is usually gathered on a common multiply master roll.

The processing step from the raw tissue that has already been optionally wound up in several plies to the finished tissue product occurs in processing machines which include operations such as repeated smoothing of the tissue, edge embossing, to an extent combined with full area and/or local application of adhesive to produce ply adhesion of the individual plies (raw tissue) to be combined together, as well as longitudinal cut, folding, cross cut, placement and bringing together a plurality of individual tissues and their packaging as well as bringing them together to form larger surrounding packaging or bundles. The individual paper ply webs can also be pre-embossed and then combined in a roll gap according to the foot-to-foot or nested methods.

## EXAMPLES

In the description of the invention and in the following examples the following test methods were used to evaluate the chemical pulps according to the invention.

#### 1) Producing the test sheets

The test sheets (having a basis weight of approx. 80 g/m<sup>2</sup>) were made in accordance with ISO 5269-2: August 1998). Before being tested in terms of physical properties e.g. by means of the tensile test, the thus obtained test sheets were always conditioned for a duration of at least 12 hours in a standard climate at a temperature of (23±1)° C and a relative humidity of (50±2)% in accordance with DIN EN 20187; November 1993, paper, cardboard and pulp, a standard climate for pretreatment and testing and a method of monitoring the climate and pretreatment of samples, November 1993 (see ISO 187 : 1990).

#### 2) Breaking length (Dry)

The breaking length was determined using a dry test sheet produced according to 1) following a process described in Zellcheming V/12/1957.

#### 3) Tear Strength (Dry) according to Elmendorff

Tear strength was determined according to Elmendorff using a test sheet produced according to 1) following a process described in DIN 53128.

#### 4) Kappa number

The kappa number is determined according to DIN 54357 (August 1978)

#### 5) WRV (water retention value)

The WRV is determined in the following way.



The principle of determining the WRV is based on centrifuging swollen pulp samples at room temperature in a special-purpose centrifuge beaker with 3000-fold gravitational acceleration. The WRV in percent (mass portions in percent) indicates the portion of water in the sample that cannot be centrifuged.

The implementation followed the German *Zellcheming* Code of Practice IV/33/57 (issued on January 1, 1957)

- A fibrous material treated with excess water as a swelling agent is taken.
- The tubes for the centrifuge inserts are filled to about 2/3 of the volume with the moist pulp sample without pressing firmly.
- A triple determination is to be performed each time.
- The tubes are inserted into the centrifuge beaker.
- Centrifuging conditions: 15 min at 4800 rpm
- After the centrifuge comes to a standstill, the tubes are taken out and the centrifuged substance immediately transferred with the aid of pincers as completely as possible into the weighing bottles previously dried at 103°C and tared at room temperature where they are weighed (remove glass spheres beforehand)
- The samples are now dried for at least 6 hours in the circulating-air drying cabinet, immediately seal when taking them out and allow them to cool in the desiccator. Now reweigh.

The calculation is made on the basis of the following equation:

$$\text{WRV} = \frac{(W-D)}{D} \times 100$$

D

where  $W$  = the weight of the moist substance,  $D$  represents the dry weight of the substance; and  $W$  minus  $D$  = the weight of the absorbed water.

#### 6) Dry Weight

The weight values that are given as “dry weight” relate to dried material, lignocellulosic material, pulp, paper, or nonwoven (product) that was dried at 105° C until constant weight was achieved.

#### 7) Freeness value

The freeness value (in °SR) was measured according to DIN-ISO 5267/1; March 1999.

#### 8) Degree of Brightness

The degree of brightness (in %) was determined according to ISO following SCAN C11:1975.

#### Example 1

Pine chips of a width of 10 to 25 mm, a length of 13 to 35 mm and with a thickness of 1 to 10 mm were pulped in a magnesium bisulfite solution (free  $\text{SO}_2$  as hydrogen sulfite or sulfite-bound  $\text{SO}_2$ ) having a total  $\text{SO}_2$  content of 23.6 % by weight/wood (dry weight) and a magnesium content measured as  $\text{MgO}$  of 7 % by weight/wood (dry weight) at an initial pH of 1.7 and temperature of 138° C. The wood-to-liquor ratio was 1:3.5. The warming to the maximum temperature of 138°C took 30 minutes. The temperature was maintained at the maximum level for a total of 4.5 hours (270 minutes). Once the defibration point was reached, cooling to room temperature required 60 minutes. The resulting pulp was separated from waste liquor, washed with water, and dried, yielding 58.2 % (dry weight) relative to the wood used, at a kappa number of 52.2 and a degree of brightness of 46.1 %

ISO. The breaking length of the unbeaten (= freeness value of 14° SR), unbleached pulp was 10.3 km at a tear strength according to Elmendorff of 87 cN relative to 100 g/m<sup>2</sup>.

The washed pulp subsequently was subjected to complexing treatment, being contacted at a temperature of 60° C for a period of 30 minutes with 2 kg/t of complexing agent DTPA at a density of 3 % (unless otherwise stated, the data given in kg/t in Examples 1 and 2 consistently refers to the dry weight of pulp). The pH value was set at 5.2 for the complexing treatment with H<sub>2</sub>SO<sub>4</sub>. Then the pulp was bleached in aqueous solution containing 50 kg/t of hydrogen peroxide and 15 kg/t MgO (at a density of 10 %) for a reaction time of 360 minutes and at a reaction temperature of 70° C. This was followed by an additional complexing treatment under the same conditions as described earlier, and subsequently by a second oxidizing bleaching with 50 kg/t hydrogen peroxide and 22.5 kg/t sodium hydroxide (at a density of 10 %). A total of 50 kg/t of peroxide was consumed in the two steps.

Finally, the resulting pulp was bleached for the last time, reduced with formamidinosulfinic acid (FAS). In the FAS step, 5 kg/t formamidinosulfinic acid was used at a temperature of 90° C and density of 10 % for a period of 60 minutes.

Following treatment with complexing agents and each bleaching step, the pulp was washed with water.

The degree of brightness of the resulting pulp was recorded at 85.9 % ISO. The yield (dry weight) of the pulp obtained after the bleaching sequence was 95.2 % by weight relative to the dry weight of the pulp subjected to the bleaching sequence. The bleached pulp had a breaking length of 9 km and a tear strength according to Elmendorff of 102.4 cN relative to 100 g/m<sup>2</sup> in the unbeaten state (freeness value = 15°SR).

### Example 2

Pine chips, 10 to 25 mm wide, 13 to 35 mm long, and 2 to 10 mm thick, were pulped in a magnesium bisulfite solution containing 16 % by weight total SO<sub>2</sub>/wood (dry weight) and

6.2 % by weight MgO/wood (dry weight). The wood(dry weight)-to-liquor ratio was 1:3.7. Warming to the maximum temperature of 150°C took 60 minutes, and the pulping at this temperature lasted 270 min (4.5 h). Cooling to room temperature occurred for a period of 60 minutes. The initial pH of the cooking liquor was 3.5. The yield of pulp after separation from the waste liquor, washing with water, and drying was 58.9 %, at a kappa number of 60.2 and degree of brightness of 47.8 % ISO. The unbeaten (freeness value = 14.5° SR), unbleached pulp had a breaking length of 10.8 km and a tear strength according to Elmendorff of 96.8 cN relative to a weight of 100 g/m<sup>2</sup>.

This pulp was subjected to the same bleaching sequence as that in Example 1, and attained a degree of brightness of 83.3% ISO. A total of 38 kg/t peroxide was consumed in this bleaching sequence. The yield (dry weight) after the bleaching sequence relative to the yield of pulp (dry weight) after pulping was 95.6 %. In the unbeaten state (freeness value = 15°SR), the bleached pulp had a breaking length of 9.4 km and a tear strength according to Elmendorff of 99.5 cN relative to 100 g/m<sup>2</sup>.

The pulp, pulped and bleached according to the invention, and/or any paper produced from such are characterized by an excellent combination of degree of brightness and strength properties. In contrast to other pulp having similar residual lignin contents, the pulp according to the invention has a high stability in degree of brightness.